SEASONAL TREND OF THE PHYSICO-CHEMICAL CHARACTERISTICS OF PM2.1: A STUDY BY SEM /EDX AND XPS IN AN URBAN AREA OF ROME

B. De Berardis[1], L. Arrizza[2], M. Inglessis[1], M. Mosca[1] and L. Paoletti[1]

[1]Istituto Superiore di Sanità
[2]Centro di Microscopia Elettronica dell'Università dell'Aquila

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INTRODUCTION

Epidemiological studies have shown a clear association between effects on health and environmental concentrations of particulate matter, especially its fine component, that is, below 2.5 μm (PM2.5). Some studies seem to indicate a larger number of deaths and hospitalizations during summer rather than winter in correspondence with the same particulate exposition.There is wide agreement regarding the hypothesis that the factor which are determinant for the effect of particulate on public health include the chemical composition of particles and their capacity to carry potentially toxic substances (such as organic substances or metallic composts) adsorbed on their surface. The aim of the present research was to study the PM2.1 composition and its physico-chemical characteristics in the city area of Rome over the course of a year by analysing, specifically the role of pollution carrier of carbonaceous particulate particularly for sulphates and organic compounds.

Materials and methods

Particulate was collected between December 2000 and December 2001 at a site near the city centre of Rome, with heavy motor traffic, by an eight-stage cascade impactor (Andersen particle fractionating sampler) with a pre-separator stage able to eliminate particles with aerodynamic diameter > of 10 μm. In this study the particulate matter with aerodynamic diameter ranging from 2.1 to 0.4 μm was utilised. Together with the particulate, and at the same site, acid aerosol was collected using an annular denuder system in order to evaluate the environmental concentration of NO_3^-, NO_2^-, Cl^- and SO_4^{--} ions. Scanning electron microscopy (SEM) equipped with a thin-window system for X-ray microanalysis by energy dispersion spectrometry and photoelectron spectroscopy techniques (XPS) were used. The ion chromatography (IC) was used to measure the environmental concentration of soluble ions.

Results

The X-ray microanalysis data of single particles were analysed using hierarchical cluster analysis (HCA) to classify the particles into groups with similar chemical composition and to determine the principal components of the particulate.It was possible to classify the particulate into four principal groups or particle "clusters": carbon rich particles, soil erosion particles, sulphates, and metallic particles. Figure 1 shows the average abundances of the identified "clusters" calculated in summer and winter.
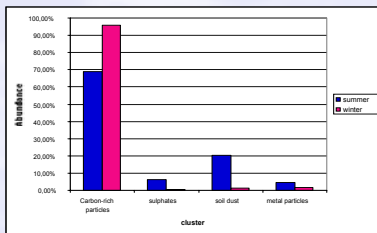

Figure 1. Average abundances of principal components in the PM2.1

Particles from soil or building material erosion (silica, silicates, carbonates) represented 4% in winter and more than 20% in summer because of the alumino-silicates carried by the wind over the sea from North Africa. Sulphates, mainly composed by Ca-sulphates can reach at most 7-8% of the total amount. Carbon rich particles, mainly resulting from vehicular traffic and, during winter, from heating systems, made up 66 to98% of the particulate depending on the season, and was more abundant in winter. Observations performed with high resolution SEM and TEM show that such particles constitute of a large number-hundreds of thousands-of aggregates of carbonaceous microsferules (Figure 2)
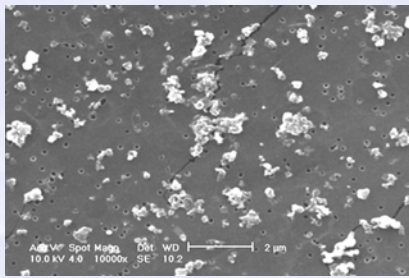

Figure 2. Carbon- rich particle aggregates. SE image (10000x)

On a varying percentage of such particles On a varying percentage of such particles, the X-ray microanalysis showed traces of S and more rarely, of alkaline metals, such as Na and K. This results was attributed to the ability of carbonaceous particles to act as vehicles for sulphur compounds, i.e. ammonium and alkaline metal sulphates, produced by SO_2 photochemical oxidation catalysed by the particles themselves. The XPS spectrum in the S_{2p} region (169-170 eV) confirm that the sulphur composts present in the PM2.1 are constituted essentially by the SO_4^{--} anion. Data for S concentration in PM2.1 obtained by XPS show that such concentrations increase from winter to summer, more than doubling from about 4% in weight of fine particulate to over 9%. (Figure 3a).
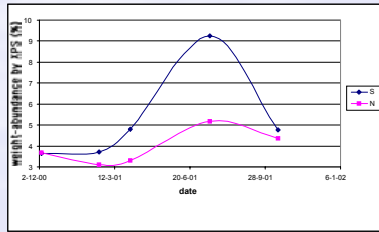

Figure 3a. Trends of sulphur and nitrogen weight-abundance in PM2.1 estimated by XPS

A similar increase is seen in the SEM data for the abundance of sulphate and carbon particles which carry S (Figure 3b). Sulphur and nitrogen abundances, estimated by XPS in the solid phase, appear closely correlated (R=0.88) each other and highly seasonal with an evident maxim in the summer (Figure 3a); this results suggest that the nitrogen observed could be present in the PM2.1 mainly as stable ammonium sulphate.
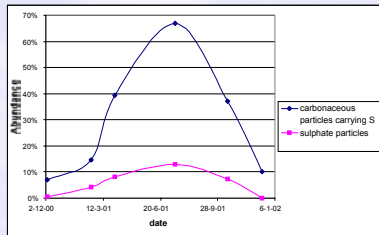

Figure 3b. Seasonal trend of sulphates and carbonaceous particles carrying S obtained by SEM

Moreover sulphate and nitrate ion concentration, determined by IC appear significantly higher during winter and the trend observed in the gaseous phase mirrors the results obtained for the sulphur compounds in the solid particulate phase (Figure 4)
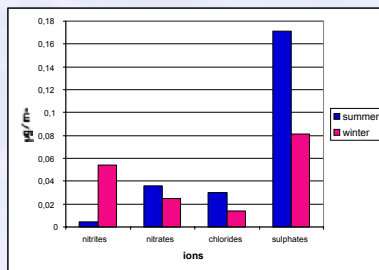

Figure 4. Average concentrations of nitrates, nitrites, sulphates and chlorides identified by IC

The XPS spectrum in the C1s region (286-290 eV) (Figure 5) show the presence of several form of oxidised carbon (organic carbon) driven by graphitic particles.
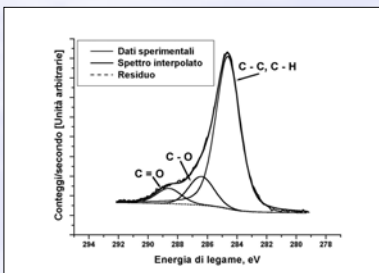

Figure 5. Three different states of Carbon obtained by deconvolution of high-resolution XPS spectra of C1s region

Figure 6 shows the trend of the ratio of Oxcarbon to total Oxygen (Oxcarbon/Oxtotal) together with the oxygenated carbon trend evaluated directly by deconvolution of C signal. Both trends show an increase of the oxygenated carbon in PM2.1 during winter.
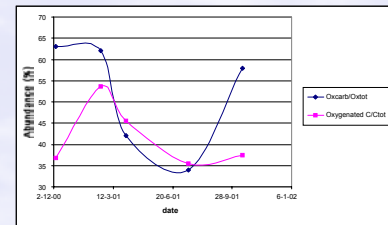

Figure 6. Seasonal trend of the ratio of oxygen bound to the carbon to the total oxygen together with the oxygenated carbon trend

Conclusions

In the urban area of Rome the principal source of pollutants emissions is the vehicular traffic and, during winter, the heating systems, mainly burning fuel or methane gas. The SEM, XPS and IC results obtained in this work seem to indicate that the antropic factors and climate pattern determine the physico-chemical PM2.1 characteristics and particularly the abundance and quality of the pollutants carried by the carbonaceous particles. The antropic factors contribute to the quality of pollutants particularly in winter by a rise of the C-rich particles together with those of the oxygenated carbon observed in the carbonaceous particulate. The climate pattern seems to determine the behaviour of the secondary pollutants carried by the solid atmospheric particulate: in summer, characterised by atmospheric stability, high pressure and humidity, we observed an increasing concentration of sulphate ions and a rise of the abundance of sulphate and carbon particles which carry S